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Key Points:
- ^{14}C analyses were performed on specific *n*-alkanes and *n*-alkanoic acids preserved in lacustrine sediments
- Vascular plant biomarker signatures are overprinted by aquatic sources and/or soil storage
- Plant wax proxies can be biased and must be chosen carefully

Supporting Information:
- Supporting Information S1

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Plant Wax *n*-Alkane and *n*-Alkanoic Acid Signatures Overprinted by Microbial Contributions and Old Carbon in Meromictic Lake Sediments

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Abstract Specific *n*-alkanes and *n*-alkanoic acids are commonly used as biomarkers in paleoenvironmental reconstruction, yet any individual homologue may originate from multiple biological sources. Here we improve source and age controls for these compounds in meromictic systems by measuring the radiocarbon (^{14}C) ages of specific homologues preserved in twentieth century Lake Pavin (France) sediments. In contrast to many studies, ^{14}C ages generally decreased with increasing carbon chain length, from 7.3 to 2.6 ka for the C_{14}-C_{30} *n*-alkanoic acids and from 9.2 to 0.3 ka for the C_{21}-C_{33} *n*-alkanes. Given a known hard water effect, these values suggest that aquatic microbial sources predominate and contributed to most of the homologues measured. Only the longest chain *n*-alkanes exclusively represent inputs of higher plant waxes, which were previously sequestered in soils over centennial to millennial timescales prior to transport and deposition. These findings suggest that biomarker source and age should be carefully established for lacustrine settings.

1. Introduction

Being universally biosynthesized and generally well preserved in recent and geologic sedimentary settings, straight-chain alkyl lipids such as *n*-alkanes and *n*-alkanoic acids (fatty acids) represent valuable organic geochemical tools for investigation and reconstruction of past environments. Their distributions and carbon and hydrogen stable isotopic compositions are used as proxies for vascular plant inputs to sediments (e.g., Schwark et al., 2002; Street-Perrott et al., 2007), changes in higher plant community structure (Castañeda et al., 2007; Huang et al., 2001), and precipitation (Makou et al., 2007; Schefuß et al., 2005; Tierney et al., 2010), to name some of the most common paleoclimate applications. It is commonly assumed when using these compound classes for paleoclimate reconstruction that the longest carbon chains (e.g., $\geq C_{26}$) are predominantly derived from terrestrial vascular plants (following source characterization by Eglinton & Hamilton, 1967), while shorter homologues (e.g., $\leq C_{21}$) are produced ubiquitously and thus primarily by aquatic organisms in marine and lacustrine environments. While this assumption may be valid in some settings, caution is warranted regarding its broad application because several studies have suggested the potential for bacterial contributions to sedimentary long-chain *n*-alkanoic acids, at least up to C_{30} (Bovee & Pearson, 2014; Gong & Hollander, 1997; Summons et al., 2013; Volkman et al., 1988), as well as production of long-chain *n*-alkanes (e.g., C_{31} and C_{33}) by phytoplankton (e.g., Freeman et al., 1994). Ultimately, such universality and the high preservation potential (Hoefs et al., 2002) of *n*-alkanes and *n*-alkanoic acids pose two fundamental problems: positive source attribution is difficult, and potentially long residence and transport times prior to definitive deposition can cause temporal offsets between these compounds and their host sediments (e.g., Douglas et al., 2014). Here we investigate the radiocarbon composition of these compounds in sediments from a meromictic lake known to be rich in bacterial and archaeal life (Lehours et al., 2007) in order to specifically address both of these concerns.

Compound-specific radiocarbon analysis (CSRA) can be used to resolve biomarker source and transport uncertainties, provided that the ^{14}C composition of assimilated carbon is known (Drenzek et al., 2007; Pearson & Eglinton, 2000; Tao et al., 2015). This technique, as used here, consists of isolating and concentrating individual compounds occurring in a complex mixture of sedimentary organic carbon (OC) then measuring their ^{14}C abundance by accelerator mass spectrometry (AMS) (Eglinton et al., 1996, 1997). It has been used

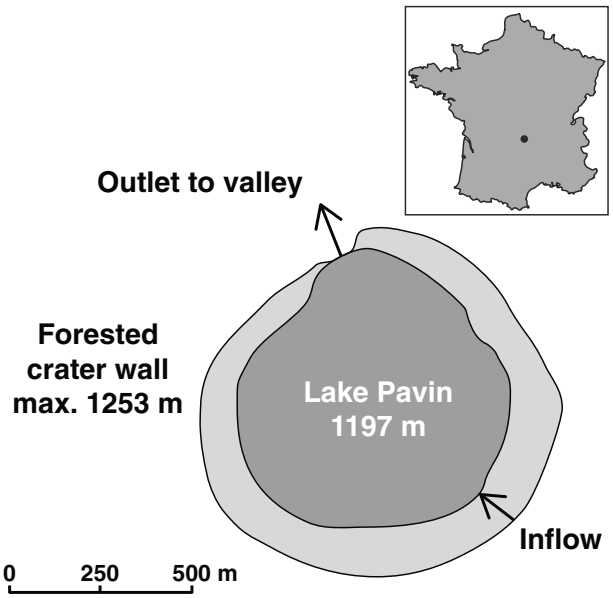

Figure 1. Lake Pavin (45°30′N, 2°53′E) geographical setting including surface water inflow and outflow. The crater walls are shaded in light gray.

successfully to further our understanding of biomarker sources and carbon cycling in marine and fluvial environments, most notably showing that refractory compounds such as alkenones, *n*-alkanes, and *n*-alkanoic acids can exhibit millennial-scale environmental residence and transport times prior to sedimentary deposition (Drenzek et al., 2009; Feng et al., 2015; Galy & Eglinton, 2011; Mollenhauer et al., 2003; Ohkouchi et al., 2002; Schefuß et al., 2016; Smittenberg et al., 2006; Tao et al., 2015; Uchida et al., 2001). The resulting biomarker-sediment age differences can complicate the spatiotemporal context of paleoclimate records.

To date, comparatively few such radiocarbon investigations have been performed in lake settings, despite the prevalent use of OC preserved in lacustrine sediments for paleoclimate reconstruction (e.g., Huang et al., 2001; Sachs et al., 2009; Shanahan et al., 2015; Tierney et al., 2010). Thus far, the range of age offsets characteristic of different compounds and lake settings remains poorly constrained. Several studies based on CSRA have so far revealed complicated, site-specific patterns of OC cycling and transport across terrestrial and lacustrine reservoirs. Uchikawa et al. (2008) found reasonably good age agreement between long-chain (C_{27}-C_{33}, odd-numbered chains) *n*-alkanes and higher plant macrofossils in a sediment core from a Hawaiian karstic pond, suggesting that these compounds could be suitable for independent age scale generation. In contrast, Douglas et al. (2014) determined centennial- to millennial-scale age offsets between long-chain (C_{26}-C_{32}, even-numbered chains) *n*-alkanoic acids and terrigenous macrofossils preserved in a sediment core from Lake Chichancanab in Mexico, consistent with a source of aged OC from soil erosion. In order to yield sufficient amounts of carbon for CSRA, both of these investigations generated ^{14}C ages from pooled biomarker samples of four compounds each, risking mixing of OC from different sources (i.e., terrestrial and aquatic). The down-core study of Gierga et al. (2016) in Lake Soppensee (Switzerland), which featured radiocarbon analysis of some individual long-chain *n*-alkanes, further suggested that the extent of terrestrial soil storage can change over time. In the present investigation, we were able to isolate a greater number of individual homologues for radiocarbon analysis than in previous lacustrine studies, contributing enhanced molecular-isotopic detail and allowing further inference of OC source and transport in a meromictic lake setting.

2. Study Site and Sampling

Lake Pavin is a meromictic crater lake, or maar, located in southern central France on the Massif Central (Figure 1). A depth of 92 m, small surface area, and the presence of steep crater walls limit wind-driven mixing to about the upper 60 m, below which the waters are permanently anoxic (Albéric et al., 2013). Small streams draining the neighboring Puy de Montchal slopes flow into the south end of the lake and surface waters outflow into a channel at the north end. Magmatic gases (Aeschbach-Hertig et al., 1999) and groundwater (Schettler et al., 2007) likely discharge directly into the lake waters, contributing CO_2, nutrients, and other chemical species. The crater walls, which rise steeply ($>$ 45° in some places) to ~ 50 m above the lake and are forested with deciduous trees (notably beech) and conifers, define a small topographic catchment (0.36 km^2) (Chassiot et al., 2016) and thus a limited source of terrestrial OC through mechanical soil erosion and surface runoff. Abundant rock falls and tree throw attest to intense mechanical erosion of the thin crater wall soils. Sedimentary pollen assemblages from Lake Pavin are consistent with strong local OC contributions, especially from within the crater, along with distal aeolian inputs from Mediterranean habitats (Stebich et al., 2005). Aquatic macrophytes are not well represented in the modern Pavin ecosystem.

We performed compound-specific radiocarbon and stable carbon isotopic ($\delta^{13}C$) measurements on a near-surface sediment sample (10–30 cm) collected from the lake depocenter at 92 m water depth. An updated Lake Pavin sedimentary chronology, developed from radiocarbon dating of a recently collected core and comparison with that of Schettler et al. (2007), suggests an age range of 1930–1985 A.D. for the 10–30 cm

Table 1
^{14}C and ^{13}C Analytical Results

Sample	Age (^{14}C years)	^{14}C error (± years)	$\delta^{13}C$ (‰)[a]
Bulk analyses			
Soil	−970	80	–
Lake POC_{susp} (4 m)	1580	80	–
Sediment (10–30 cm)	6220	220	–
Water column data[b]			
DIC (inflow)	−400	–	–
DOC (5 m)	1900	60	–
DIC (10 m)	6630	40	–
DIC (70–90 m avg.)	9250	40	–
Sediment n-alkanoic acids			
$C_{14} + C_{18}$	7280	220	−29.1
C_{16}	7230	140	−30.1
C_{22}	7530	170	−31.2
C_{24}	6560	100	−26.1
$C_{26:1}$	7460	150	−12.6
C_{26}	6020	110	−26.0
C_{28}	4290	110	−30.9
C_{30}	2610	160	−31.4
Sediment n-alkanes			
C_{21}	9160	160	−37.2
$C_{23} + C_{25}$	6570	160	−29.9
C_{27}	3080	200	−31.0
C_{29}	740	610	−32.2
$C_{31} + C_{33}$	300	430	−34.1
Even chain lengths	4830	350	–
Soil n-alkanes			
$C_{21} + C_{23} + C_{25}$	140	110	−33.3
C_{27}	−920	60	−31.7
$C_{29} + C_{31} + C_{33}$	920	230	−34.4

[a]Errors ranging from 0.0 to ±0.8‰. [b]From Albéric et al. (2013).

interval (Chassiot et al., 2016), meaning that the upper portion of the sample was deposited during or after the period of nuclear weapons testing. However, age scale uncertainties present the possibility, although unlikely, that the entire sediment interval was deposited prior to the bomb test era. We also collected a surface soil sample (0–5 cm) from the thin layer covering the eastern crater wall and a suspended particulate organic carbon (POC_{susp}) sample (31 L of lake water pumped through a precombusted Whatman 142 mm GF/F filter) from 4 m water depth, both of which were analyzed for bulk OC ^{14}C. Compound-specific radiocarbon (and $\delta^{13}C$) measurements were performed for *n*-alkanes in the surface soil sample in order to constrain potential catchment residence times prior to erosion and transport to the lake.

Compound isolation and CSRA were based on the approaches of Eglinton et al. (1996) and Tao et al. (2015). The analyzed compounds and results are presented in Table 1, and details concerning sample preparation, analysis, and data treatment (Christl et al., 2013; Shah & Pearson, 2007) are provided as supporting information (Text S1). Individual homologues were combined in cases where compound abundances were too low for reliable AMS measurement (i.e., about 5 μg C or less), with care to pool homologues only of similar chain lengths. All data are expressed in ^{14}C years rather than calendar age because biological source is expected to exert the dominant influence on OC radiocarbon composition in Lake Pavin sediments. Conventional correction methods using the oxalic acid reference material define a "modern" ^{14}C age (0 year) as 1950 A.D.

3. Results and Discussion

3.1. Sedimentary Lipid Ages and Lake OC Cycling

The *n*-alkane and *n*-alkanoic acid distributions observed in the Lake Pavin near-surface sediments (Figure 2) are typical of those preserved in many lacustrine or marine settings, with a broad carbon chain length distribution suggestive of both terrestrial vascular plant and aquatic organismal sources. Among the *n*-alkanoic acids, a predominance of C_{16} and C_{22}, as well as the robust presence of several monounsaturated homologues ($C_{16:1}$, $C_{18:1}$, $C_{24:1}$, and $C_{26:1}$), suggests substantial sedimentary inputs of aquatic microbial OC. Nearly all of the homologues in both compound classes exhibit old radiocarbon ages, ranging from 7.5 to 2.6 ka (ka = 10^3 years) for the *n*-alkanoic acids and from 9.2 to 0.3 ka for the *n*-alkanes. Ages generally decrease with increasing carbon chain length, most clearly for the *n*-alkanes (Table 1 and Figure 2). The *n*-alkanoic acid ages are more uniform than those of the *n*-alkanes, with comparatively older values at higher chain lengths that never approach a modern value. Bulk sediment OC has an age of 6.2 ka, suggesting a mixture of material spanning the age range measured for both compound classes.

Broadly defined potential sources of OC to Lake Pavin sediments include the following: vascular plant matter (Stebich et al., 2005) delivered either directly or after soil storage, phytoplankton and zooplankton in near-surface waters, and a rich bacterial and archaeal community inhabiting the water column and sediments (Lehours et al., 2007). Because of characteristic ^{14}C values to be expected based on the metabolism and ecological setting specific to these different organismal groups, we are able to infer the predominant sources for each of the dated lipids. The robust negative ages determined for the crater wall soil bulk OC and C_{27} *n*-alkane (Table 1) confirm the presence of bomb-derived (post-1950) radiocarbon in the Lake Pavin catchment, likely associated with higher plant photosynthesis. A source of postbomb carbon to the lake surface is also demonstrated by a dissolved inorganic carbon (DIC) ^{14}C age of −400 years for the southern surface inflow waters (Albéric et al., 2013). A measured age of 1.6 ka for POC_{susp} at 4 m depth in the lake suggests the value expected for phytoplankton-derived biomarkers, although Albéric et al. (2013) determined an older plankton (0–10 m) age of 3.6 ka. These old POC_{susp} and plankton values, along with upper-water column

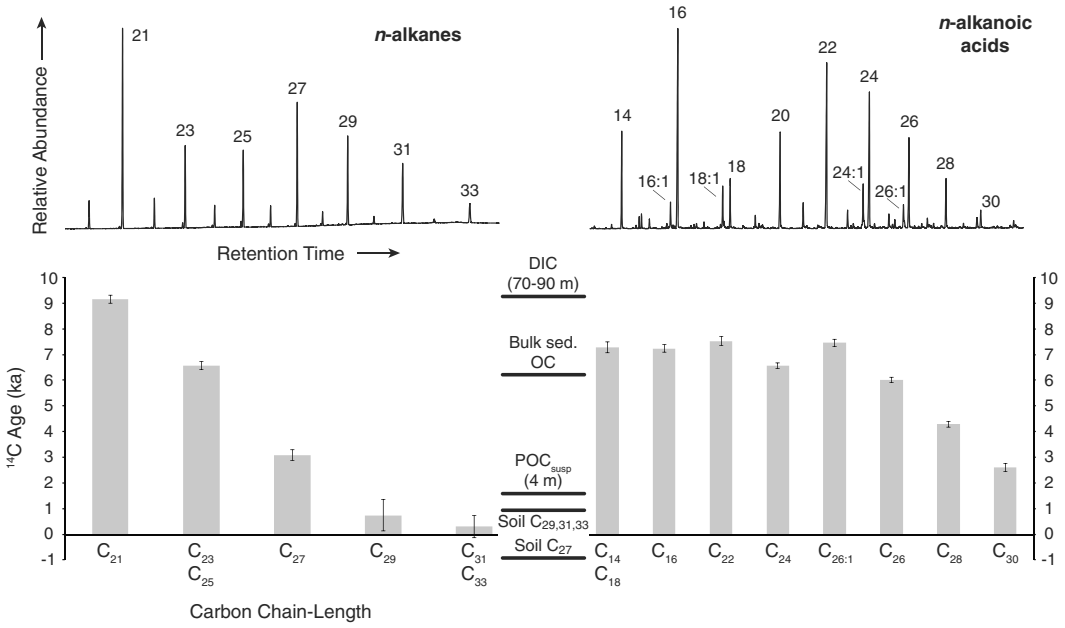

Figure 2. (top row) Chromatograms of the lake sediment *n*-alkane and *n*-alkanoic acid fractions prepared for PCGC separation. Carbon chain lengths are indicated. (bottom row) Sediment CSRA results reported in ^{14}C age. Several independent ^{14}C values are shown for comparison: a DIC average value over 70–90 m water depth (Albéric et al., 2013), bulk sediment OC, lake water POC_{susp} from 4 m depth representing the phytoplankton signal, and soil *n*-alkane CSRA values for C_{27} and $C_{29+31+33}$. Negative values are attributed to bomb-derived radiocarbon.

dissolved organic (DOC, 5 m) and inorganic (DIC, 10 m) carbon measurements of 1.9 and 6.6 ka (Albéric et al., 2013), respectively, suggest that the modern inflow waters are well diluted near the surface by aged carbon from within the mixolimnion (0–60 m). Due to the lake's permanent stratification and potential magmatic and groundwater carbon sources, the deeper microbial communities have access to DIC that is strongly ^{14}C depleted, with a corresponding average ^{14}C age of 9.3 ka between 70 and 90 m (Albéric et al., 2013). These disparate ^{14}C end-members within the lake and its catchment (Figure 2) suggest that the metabolic carbon source used by each biological precursor group will be the primary influence on biomarker apparent age within a given sediment horizon.

The ^{14}C age offsets between *n*-alkanes and *n*-alkanoic acids of similar carbon chain length are striking, especially considering that the higher chain length homologues in both compound classes are thought to be derived from plant leaf waxes. At the shortest carbon chain lengths, they both exhibit ages approaching the deepwater DIC end-member (Figure 2), suggesting a primarily microbial origin. This is consistent with the microbially rich and diverse Lake Pavin ecosystem and common short-chain lipid source attribution (e.g., Gong & Hollander, 1997). However, *n*-alkanoic acid ages do not decrease as sharply with increasing chain length as those of the *n*-alkanes (Figure 2); the C_{30} *n*-alkanoic acid is 2.3 ka older than the *n*-alkanes of comparable carbon chain length (C_{31} + C_{33}). This discrepancy is in sharp contrast to similar studies in the literature (Kusch et al., 2010; Pearson et al., 2001; Tao et al., 2015), in which sedimentary *n*-alkanes are older than co-occurring *n*-alkanoic acids due to fossil OC inputs. Likewise, long-chain *n*-alkanes can be considered as the more refractory (slower turnover times) of the two compound classes (e.g., Galy & Eglinton, 2011; Smittenberg et al., 2006). Here the data suggest that the longest-chain *n*-alkanes (C_{29}-C_{33}) and *n*-alkanoic acids (C_{28}-C_{30}) are derived primarily from different sources; the former are representative of predominantly higher plant wax inputs with relatively recent ^{14}C ages, while the latter also incorporate extensive aquatic (microbial) inputs characterized by older radiocarbon ages due to a hard water effect.

We hypothesize that the microbial community in Lake Pavin dominates inputs of sedimentary *n*-alkanoic acids up to about C_{26} and including $C_{26:1}$ and also synthesizes homologues at least as long as C_{30}. In this

respect, our CSRA results are consistent with previous studies of *n*-alkanoic acid abundance and stable carbon isotopic composition that suggest microbial derivation of long-chain homologues (Bovee & Pearson, 2014; Gong & Hollander, 1997; Summons et al., 2013; Volkman et al., 1988). Compound-specific $\delta^{13}C$ measurements of the Lake Pavin sedimentary *n*-alkanoic acids lend support to this interpretation, as the values obtained for C_{28} and C_{30} are similar to those of the shortest (C_{14}-C_{22}) homologues (Table 1). Here changes in the relative contributions of aquatic and terrestrial sources to each homologue are better interpreted from the CSRA data, which suggest increasing—but never predominant—leaf wax-derived contributions to the C_{28} and C_{30} *n*-alkanoic acids.

Unlike the *n*-alkanoic acids, the longest-chain *n*-alkanes approach modern radiocarbon ages (defined as 1950 A.D. or later by conventional dating methods), and their age profile (Figure 2) suggests a robust increase in higher plant influence with increasing carbon chain length. No submerged macrophytes were observed around the lake, and thus, they are not likely contributors to the middle chain length (C_{23} and C_{25}) *n*-alkanes (Ficken et al., 2000). There is essentially no evidence of a bomb ^{14}C signal in any of the sedimentary compounds we analyzed, including the C_{31} and C_{33} *n*-alkanes (300 ± 430 years), which are likely derived from vascular plant waxes in the catchment. Possible explanations for the lack of a clear bomb spike in these "terrestrial" biomarkers include the following: intermediate storage of higher plant-derived OC in the Lake Pavin crater soils, a mixed ^{14}C signal arising from microbial production of these compounds within the lake, sediment age scale errors, and contamination by fossil OC (i.e., organic matter derived from petroleum or ancient sediments). We measured the age of the pooled even chain length *n*-alkanes (C_{22}-C_{32}), which are characteristic of petroleum or kerogen sources when observed in relative abundance (with respect to the odd chain length homologues), to test for such contamination. An anomalously old age would indicate derivation from fossil OC (e.g., Tao et al., 2015) as ancient organic matter contains no remaining radiocarbon. However, the ^{14}C age of 4.8 ka determined for the pooled even carbon number chains is intermediate between the other measured *n*-alkane ages (Table 1), arguing against significant contributions of fossil OC, including petroleum contaminants. This apparent lack of fossil input is in contrast to other studies from more open environments such as rivers and continental shelves, where ancient sediments can be an important OC source (Drenzek et al., 2007; Tao et al., 2015). The other possible explanations for the centennial-scale C_{31} and C_{33} *n*-alkane age are addressed below.

3.2. Soil *n*-Alkane Ages

CSRA of *n*-alkanes in the soil sample allows us to directly investigate soil OC storage and infer plant wax transport dynamics in the catchment. The results suggest the presence of a complex mixture of modern (postbomb) and aged OC that can be delivered to lake sediments through erosion. The C_{27} homologue dominates the soil *n*-alkane profile, which exhibits relatively minor contributions of other odd chain length homologues (supporting information Figure S1). This distribution is typical of beech tree leaves and the soils underlying them (Marseille et al., 1999) and is consistent with a dominant presence of beech trees in the Lake Pavin catchment (Stebich et al., 2005). While gymnosperm trees are also abundant on the crater walls, these typically produce very low abundances of *n*-alkanes (Diefendorf et al., 2011). We thus conclude that plant wax *n*-alkanes in catchment soils are principally derived from angiosperm (e.g., beech) trees. An individual apparent ^{14}C age of −920 years (postbomb) was obtained for the dominant C_{27} homologue, the grouped shorter-chain (C_{21}, C_{23}, and C_{25}) *n*-alkanes had an age of 140 ^{14}C years, and the grouped longer-chain (C_{29}, C_{31}, and C_{33}) *n*-alkanes exhibited a much older ^{14}C age of 920 years (Table 1). The recent ^{14}C age observed for C_{27} implies abundant direct input of fresh beech leaf waxes to surface soils. However, beech leaves produce relatively minor amounts of *n*-alkanes longer than C_{27} (Marseille et al., 1999), and thus, the presence of these homologues in Lake Pavin soils can be attributed primarily to other sources. This inference is supported by a 1–3‰ $\delta^{13}C$ offset between C_{27} and the longer-chain soil *n*-alkanes (Table 1). The date obtained for the long-chain homologues instead suggests the presence of a separate soil OC pool aged about 1,000 years, which likely includes a mixture of inputs such as aged plant waxes from mixed vegetation, fungi, and other soil microorganisms (Nguyen Tu et al., 2011). van der Voort et al. (2016) noted enhanced spatial OC ^{14}C variability in soils occurring on steep slopes, attributable to soil mixing through increased physical erosion, and tree throw in particular. We suggest that the same processes, operating on the steep Lake Pavin crater slopes, produced a complex soil *n*-alkane mixture bookended by fresh leaf waxes and 1,000 or more year old OC.

3.3. Sources of *n*-Alkanes in Lake Pavin Sediments

The centennial-scale age (300 ± 430 years) observed for the Lake Pavin sediment C_{31} and C_{33} *n*-alkanes and the lack of a predominant bomb spike are most readily explained by erosion of catchment soils and transfer to the lake. Sediment varves attest to the annual deposition of higher plant OC (Schettler et al., 2007), and a sediment pollen record also suggests rapid delivery of local terrestrial inputs (Stebich et al., 2005). Thus, there is a continuous transfer of soil OC to the lake and a direct comparison can be made between the *n*-alkanes occurring in each setting. The soil *n*-alkane radiocarbon analyses define two distinct pools of OC that are subject to erosion: a fresh leaf wax component as evidenced by the beech tree inputs (C_{27}) and OC sequestered in soils with an age of about 1,000 years, as defined by the longest homologues. It is important to bear in mind that the ^{14}C age determined for the long-chain soil homologues is itself a mean value, likely representing a broad distribution of both recent and even older OC. Compound-specific $\delta^{13}C$ measurements support the interpretation of a soil erosion source for the longest-chain lake sediment *n*-alkanes, with similar values observed for each setting (−34.4 and −34.1‰, respectively). The sediment C_{31} and C_{33} *n*-alkane age of 300 years represents a mixture of the fresh (postbomb) and old (920 years) OC components in catchment soils. Error bars allow for a range of mixing proportions, but the lack of a strong bomb spike in the sediment sample necessarily invokes the presence of a pre-aged (centennial- to millennial-scale) OC component.

The interpretation of a predominant soil source for the C_{31} and C_{33} *n*-alkanes in Lake Pavin could be biased by potential aquatic microbial production of these compounds. It is possible that a purely terrestrial homologue is not present in Lake Pavin sediments and that there are minor microbial contributions to even the longest chains, as is inferred to a greater extent for the *n*-alkanoic acids. Abundant long hydrocarbon chains (e.g., ≥ C_{27}) have been observed in freshwater algae (Gelpi et al., 1970; Liu & Liu, 2016), and Freeman et al. (1994) proposed a possible phytoplankton source for marine C_{31} and C_{33} *n*-alkanes based on stable carbon isotopic evidence. Although the rich, microbially dominated Lake Pavin ecosystem may similarly provide a source of long-chain *n*-alkanes, compound-specific $\delta^{13}C$ measurements do not support such a conclusion. A $\delta^{13}C$ value of −34.1‰ for C_{31} and C_{33}, which is nearly the same as that of the long-chain *n*-alkanes in the catchment soils (Table 1), is not matched in the putatively aquatic short-chain homologues. The C_{21} *n*-alkane, which exhibits a ^{14}C age close to that of the deepwater DIC (Figure 2) and is thus likely derived from aquatic microorganisms living in the anoxic part of the water column (70–92 m) and/or within the sediments, has a substantially lower $\delta^{13}C$ value of −37.2‰. The C_{23} and C_{25} homologues, which also have a radiocarbon age consistent with predominantly aquatic sources, have a significantly higher $\delta^{13}C$ value of −29.9‰. These $\delta^{13}C$ results suggest a different suite of aquatic microbial sources for C_{21} and the other short-chain *n*-alkanes, and the overall differences between C_{31+33} and the shorter-chain homologues in both isotopic systems render an aquatic contribution of long-chain homologues unlikely. The paired compound-specific radiocarbon and stable carbon isotopic results presented here demonstrate how such methods are highly complementary for biomarker source identification.

3.4. Broader Implications

The Lake Pavin CSRA results are in agreement with those of Douglas et al. (2014), where a 350–1200 year age difference between codeposited plant waxes and lake sediments was observed and attributed to mobilization of old OC from catchment soils. Thus, the finding of Uchikawa et al. (2008) that lacustrine sedimentary *n*-alkanes can provide an unbiased age scale appears valid for their specific study site but cannot be applied universally. For Lake Pavin, we suggest a centennial-scale temporal offset that in fact arises from the mixing of recent and refractory (millennial-scale) pools of soil OC. As noted above, sediment core age scale errors could affect our interpretations regarding the C_{31} and C_{33} *n*-alkanes, as they allow for the unlikely possibility that the 10–30 cm sediment interval was deposited before the era of prominent nuclear weapons testing. In this case, the bomb spike would not be expected in our sample and we may have overestimated soil OC residence time. However, unexpected errors in the Chassiot et al. (2016) age scale are uncalled for; the lack of a clear bomb spike in the sediment is more readily explained by dilution resulting from delivery of the approximately 1,000 year old soil *n*-alkanes.

The compound-specific ^{14}C results presented here have important implications for the use of *n*-alkanes and *n*-alkanoic acids in paleoenvironmental and paleoclimate investigations, such as for generating leaf wax

records, at least for meromictic lakes such as Lake Pavin. We propose that the two compound classes cannot be used interchangeably as markers of vascular plant OC. The longest chain homologues of each class clearly derive from different OC sources, and the proximity of the *n*-alkanoic acids to the deepwater DIC ^{14}C end-member (Figure 2) suggests that they are dominated by aquatic microbial inputs. No *n*-alkanoic acid homologue in Lake Pavin sediments appears suitable as a plant wax biomarker. While the C_{31} and C_{33} *n*-alkanes appear to be primarily derived from the catchment vegetation and would be the clear choice for generating plant wax-based paleoclimate records, these compounds present potential temporal biases. Centennial- to millennial-scale soil residence times may bias age interpretations and thus limit the effectiveness of increasing sampling resolution to interpret abrupt climate variability.

4. Conclusions

The present investigation employs ^{14}C primarily as a biological source indicator, shedding new light on the origin of individual *n*-alkanes and *n*-alkanoic acids in Lake Pavin. Lake ecosystems are diverse, and the same biomarker approach may not work in different settings, as evidenced by previous lacustrine CSRA investigations (Douglas et al., 2014; Uchikawa et al., 2008). Here we add detailed constraints on carbon cycling in a meromictic lake to better understand the dynamics pertinent to an ultraproductive, stratified lacustrine ecosystem. We propose that in this type of setting, sedimentary *n*-alkanoic acids may derive predominantly from aquatic microbial productivity, which produces homologues at least as long as C_{30}. We further hypothesize that *n*-alkane homologues $\leq C_{27}$ are at least partly derived from microorganisms, with an increase in the terrestrial/aquatic ratio over increasing chain lengths. Surface soils even in this steep-walled, small catchment contain approximately 1,000 year old OC, which after remobilization through erosion can produce centennial-scale temporal lags between the purely terrestrial biomarkers (C_{31} and C_{33} *n*-alkanes) and the lake sediments they are preserved in.

No perfect terrestrial biomarker was found thus far in Lake Pavin sediments, as none of the investigated compounds represent purely vascular plant-derived OC that was also rapidly delivered to the sediment. We argue that for such settings, specific *n*-alkane and *n*-alkanoic acid homologues should never be chosen a priori as source-specific biomarkers and that their origin should first be verified, for example, through isotopic analyses. Likewise, indices based on these compounds and used for source apportionment, such as P_{aq} (Ficken et al., 2000), should be employed with care. While our findings present real and problematic biases for paleoclimate reconstruction using molecular biomarkers, they also pertain to a rare and extremely productive setting. Further research, specifically ^{13}C and ^{14}C measurement of individual sedimentary biomarkers and establishment of their OC source end-member isotopic compositions, will help to constrain the possibilities within a greater diversity of lake settings.

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